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19 ABSTRACT (Continue on reverse if necessary and identify by block number) Photo-promoted hydrogenation of CO_2 at 1 atm total pressure over a number of catalysts was investigated. CO was the principal product of both the dark and photo-promoted reactions in the presence and absence of water vapor. The first batch of a Co-Mo-Al-Oxide preparation was the most active photocatalyst investigated, giving 0.35 molec. of CO per incident photon of white light and, in the presence of water vapor, a yield of CO equal to 10 times its concentration at thermal equilibrium. Studies of this system included the action spectrum for formation of CO and the dependence of rate on the CO_2/H_2 ratio, on temperature and on intensity of white light. The catalyst was a heterogeneous mixture of several phases. Subsequent batches of Co-Mo-Al-Oxide, prepared according to the original protocol, differed from the first batch in composition and were less active photocatalysts. Similar studies were carried out using pristine and platinized DeGussa P-25 TiO_2 as catalyst.			
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PHOTOASSISTED REACTION OF H_2 WITH CO_2 OVER SOLID CATALYSTS

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Summary of Research

Early work of the project [1] found that CO was the only detectable carbon-containing product of the dark reaction of CO₂ with H₂ over α -Fe₂O₃, Zn-Fe-Oxide, Co-Mo-Al-Oxide, Co-Mo-Ti-Oxide, platinized La-Ni-Oxide or platinized SrTiO₃, either in the presence or in the absence of water vapor. Under illumination by a mercury-xenon lamp with wavelengths below 350nm and above 2750nm filtered out, in the absence of water vapor CO remained the major product with minor amounts (approx. 0.1mole% of CO) of CH₄. Under the indicated illumination, in the presence of water vapor, CO was again the major product, together with approximately 0.1mole% of methane along with smaller amounts of methanol, traces of formaldehyde and 5-20 mole% of formic acid. The major result of illumination was to increase yields of CO by factors of 2 - 4.5, depending on the catalyst. The largest photo-efficiency, 0.35 molecule of additional CO per incident photon, was observed with Co-Mo-Al-Oxide. Over this catalyst, under illumination in the presence of water vapor, the yield of CO corresponded to ten times its concentration at thermal equilibrium.

On the basis of the early encouraging results obtained using Co-Mo-Al-Oxide as the catalyst, further studies involving this catalyst were pursued. These studies found that the rates of the dark and photopromoted reactions depend differently on the H₂/CO₂ ratio, that the temperature dependence is similar for the dark and photopromoted reactions, that photo-promotion of CO formation is observed with both 350-480nm and 650-1000nm light and that the rate of formation of CO varies inversely with intensity of white light. X-ray diffraction data showed that the catalyst was a heterogeneous solid composed of a number of phases. The catalyst was found to absorb over the entire wavelength range from 190 to 900nm, with prominent bands peaking below 190nm and around 300, 360, 600 and 850nm.

Plans to carry out a thorough fundamental investigation of the reaction of CO₂ and H₂ were frustrated by inability to reproduce Co-Mo-Al-Oxide catalyst with the high photoactivity of the original preparative batch which had been used in all the prior work. The several batches prepared according to the protocol used for the original batch differed also from each other and the original batch in composition as revealed by X-ray diffraction. DeGussa P-25 TiO₂ was chosen as the catalyst to be used in further studies of the hydrogenation of CO₂ to give CO, the only product formed in significant amounts over this catalyst in the dark and under illumination. Photopromotion of formation of CO was observed with H₂-rich gas mixtures and declined as the proportion of H₂ diminished. The action spectrum with H₂-rich mixtures paralleled the absorption spectrum of the catalyst and the dependence on light intensity was relatively complicated. With fluxes in the range from 1×10^{15} photons/sec/cm² to somewhat less than ten times this amount, the rate was proportional to the square root of the flux. With fluxes in the range $(10 - 38) \times 10^{15}$, rate varied linearly with flux. Photo-inhibition of production of CO was observed with CO₂-rich mixtures. A similar study of the reaction over platinized TiO₂ was also performed.

Journal Publication

[1] N.N.Lichtin, K.M.Vijayakumar and B.I.Rubio, J. Catalysis, **104**, 246-51 (1987). (also submitted as Technical Report No. 1)

Participating Personnel

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